Referee 2

We thank the referee for detailed and helpful comments which are repeated below in black text. Our replies are in blue. We note that both reviewers suggested that making quantitative statements regarding the impact of pyruvic acid photolysis on e.g. CH_3CHO or radical production was not possible given the very concise reaction scheme used. In the light of these comments we have re-done the box-modelling using a comprehensive reaction mechanism drawn from the MCM.
We have also performed quantum chemical calculations to evaluate the fate of methylhydroxy carbene, now believed to be the major product of pyruvic acid photolysis at actinic wavelengths. The manuscript has thus been substantially rewritten.

The authors use a box model to analyze data from two field studies in Hyytiala (summer-autumn of different years), examining the potential impact of pyruvic acid (PYR) photolysis on acetaldehyde and HOx radical budgets in this boreal forest area. The topic is of interest and importance, and thus relevant to ACP readership. I have some significant concerns with the work, however, mostly related to assumptions made in the box model analyses; some of these are discussed by the authors, but I think there are others that need to be addressed (particularly in the context of how quantitative the conclusions are, given the uncertainties in PYR photolysis and depositional loss and the nature of some of the approximations made). More details follow.
We have now performed a more detailed box-modelling study using the CAABA/MECCA atmospheric chemistry box model with >600 gas-phase species and ~2000 gas-phase reactions and photolysis steps. CAABA/MECCA uses a reduced mechanism based on the MCM.

One over-arching comment:

Some of the ideas explored here have already been touched upon in the authors' previous publication on this topic (Eger et al., ACP 2020), and I found that some of the questions that came to mind were actually addressed in the previous paper. I would thus like to see a clear distinction made between the two works, via the addition of a paragraph or two to the end of the introductory material to summarize the findings of the previous study, and to set the stage for what is done in this paper.
The paper has been substantially revised. Along with the detailed box-modelling we have now done, we have also performed a theoretical analysis of the fate of methylhydroxy carbene formed initially in pyruvic acid photolysis. Overlap between the papers is substantially reduced.

More detailed comments:

Is it realistic to assume a mixed boundary layer (even in daytime) for fairly short-lived vegetative emissions? Can the authors be more quantitative or descriptive of what the implications of this assumption are?
As we describe in detail, we have attempted to use realistic boundary-layer heights as this in central to the calculation of deposition velocities and emission rates for pyruvic acid and monoterpenes. If the boundary layer is not well mixed, the emission rates we derived (based on measurements close to ground level) will be biased high and the deposition losses biased

low. We now write "Further, our calculations are based on the assumption that the sources for pyruvic acid and MT emissions are evenly distributed and measurements made at ~ 8.5 m above the ground are representative of the entire boundary layer (i.e. that the boundary layer is well-mixed, including the very shallow boundary layer at night). A gradient in pyruvic acid mixing ratios at night cannot be ruled out, which would impact on our results. If the boundary layer is not well mixed, the emission rates we derived will be biased high and the deposition losses biased low. We estimate that the emission ratio (E_{pyr} / E_{MT}) in Eq. (2) is associated with an overall uncertainty of a factor ~2.

Is the chemistry in the box model sufficiently detailed to capture HOx radical budgets accurately in this complex terpene-driven system, and thus assess changes driven by PYR photolysis? In particular, could there not be multiple sources of CH3C(O)O2 radicals from the terpene chemistry that is not included in the model? Do we really know enough about terpene oxidation to rule out PYR production?
We have now performed a more detailed box-modelling study using the CAABA/MECCA atmospheric chemistry box model with >600 gas-phase species and ~2000 gas-phase reactions and photolysis steps. We now consider the formation of $CH_3C(O)O_2$ in detail, including those pathways associated with terpene degradation insofar as they are implemented in the MCM and CAABA/MECCA.

Regarding OH in the IBAIRN modeling, I did not quite follow sentences near the bottom of page 5. Am I correct that OH is modeled (not constrained), but is lowered in the model via addition of extra reactivity to match the UV/OH correlation determined in other campaigns at the site? Please clarify.
It is correct that OH was not measured during IBAIRN. However, many years of OH measurements at this site have been used to derive a simple expression that reproduces OH levels reasonably well from measurements of UVB. Our new box-model runs generate OH levels that are in agreement with those based on the UVB calculation and this is now stated in the text.

Bottom of page 6 - Do the monoterpenes (MT's) have significantly different lifetimes and, if so, can the anything be said about how averaging their loss rates might impact the analysis?
We no longer quote the average lifetime as this information is superfluous. We recognise that treating the MT non-explicitly introduces significant uncertainty into the calculation and now mention this in the text.

Page 7 - I would like to get some sense of the variability in the average diel profiles shown, particularly for the emission rates of PYR and MT (Figure 2). This variability then carries forward to the data shown in Figures S3 and S4, correct?
This is correct. We now refer to our previous paper (Eger et al, 2020) in which we plot the diel profiles of monoterpenes and pyruvic acid along with the 25 % and 75 % percentiles as an indicator of variability. To maintain clarity of presentation, we have chosen not to include this variability in the present Figure 2.

Bottom of page 7 - The data showing the T-dependence of the PYR to MT emissions ratio look quite convincing. Isn't it likely, however, that this ratio is influenced also by light levels, thus complicating the analysis of the T-dependence?
The temperature dependence is highly uncertain as it is strongly influenced by the deposition term for pyruvic acid, which is dependent on the boundary-layer (and its insolation / temperature dependent variability). In order to emphasise this we now write: "We note that

(like the values of E_{pyr}) the temperature dependence derived is strongly influenced by the insolation-dependent diel variation of the MXL height and thus carries significant uncertainty."

Page 9 - Is PAN nominally in steady-state (or close to it)? If so, I am not sure it makes sense to consider its decomposition to be a source of CH3C(O)O2 radicals?
This is correct. In evaluating our new model results, we do not consider PAN as a net source of $CH_3C(O)O_2$

Page 10/11 - I have significant misgivings about doing anything quantitative with the HUMPPA campaign data, given the absence of PYR mixing ratio data. Surely, and as stated (to an extent) by the authors, the emissions ratios (E_PYR / E_MT) could be affected by changes in temperatures, light levels, vegetation, availability of plant litter, different soil moisture content, etc. etc. I would recommend nothing more than some qualitative estimates regarding the HUMPPA campaign data, rather than any sort of quantitative analysis. Also, I realize that inclusion/exclusion of the biomass burning impacted data made little difference to the findings, but is it not quite likely that there are biomass burning sources of acetaldehyde, MTs and possible PYR during these periods that are not factored into the analysis here?
We agree that the use of pyruvic emissions derived in the autumn to the same site in the summer carries great uncertainty, and we have removed the HUMPA analysis from the paper.

Minor comments:

Page 4 - (R5) should have CO2 as the product, not CO.
Correction applied

Page 5, line 6 – IUPAC is missing the I.
Correction applied

Page 6, line 14 – Can some data be shown to demonstrate the statement made here stating that changes in the PYR mixing ratio could be reproduced by the model?
In our new box-model runs pyruvic acid was always constrained by observations. We no longer make this statement.

Pg. 7, line 9 - There is roughly a factor of two uncertainty in PYR deposition, and there is roughly a factor of four difference in the overall PYR quantum yield used in the different sensitivity studies. Thus, would not the uncertainty in the emission ratio be larger than a factor of two?
The uncertainty in the relative emission ratio depends on the contribution to losses by photolysis and by deposition. Note that uncertainty in the BL-height cancel with this approach. We have not considered the different quantum yields. We have adopted the text to clarify this.

Page 8, line 25 – I am getting different numbers for the emissions ratios than are given here (on the basis of the branch emission rates given). Please check / confirm.
The emission-ratios quoted are based on the emission rates (in µg C gdw^{-1} h^{-1}) listed in Table 2 and take into account the number of carbon atoms in pyruvic acid (3), isoprene (5) and monoterpenes (10).

Page 9, line 29 – I think you are meaning to say that the fractional contribution of the alkanes drastically decreases?
Based on the new box-model results, this text has been re-written.

Lastly, a bit of an aside: The authors might not yet be aware, but there was a presentation at the AGU a couple of months ago that appears to show the hydroxycarbene $CH_3COH + CO_2$ as the major channel at 351 nm (Osborne and co-workers). I don't think any quantum yields were reported.
We thank the reviewer for this information. The work was recently published (Samanta et al, 2021, Phys. Chem. Chem. Phys.). As this result changes the picture substantially, we have performed quantum chemical calculations on the fate of the carbene and changed box-model scenario "C" to consider carbene chemistry. This is a totally new section in the paper.